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EFFECT OF TEMPERATURE ON STABILITY OF SULFUR DIOXIDE SAMPLES COLLECTED BY THE FEDERAL REFERENCE METHOD

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This report describes an evaluation of the effect of temperature on the stability of samples collected according to the Environmental Protection Agency procedure for measurement of ambient sulfur dioxide. This evaluation was carried out over the range 35 to 278 micrograms per cubic meter of air sampled. Collected samples were found to decay at a critical temperature-dependent rate. The rate of decay increases five-fold for every 10 degree centigrade increase in temperature over the range 20 to 40 degrees. The rate of decay is independent of concentration over the range studied, and the decay reaction follows first-order kinetics. A mathematical model was developed that allows sample decay to be calculated if the temperature history of the sample is known. Temperature specifications and changes in the procedures necessary to eliminate the decay problem are proposed.

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EFFECT OF TEMPERATURE ON STABILITY OF SULFUR DIOXIDE SAMPLES COLLECTED BY THE FEDERAL REFERENCE METHOD

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ABSTRACT

This report describes an evaluation of the effect of temperature on the stability of collected samples according to the Environmental Protection Agency (EPA) reference procedure for measurement of ambient sulfur dioxide. This evaluation was carried out over the range of 35 to 278 $\mu g\ SO_2/m^3$.

Collected samples decay at a critical temperature-dependent rate. The rate of decay increases five-fold for every 10°C increase in temperature over the range 20 to 40°C. The rate of decay is independent of concentration over the range studied, and the decay reaction follows first-order kinetics.

At 20, 30, 40 and 50°C (68, 86, 104 and 122°F) SO_2 is lost at the rate of 0.9, 5.0, 25, and 74 percent per day, respectively.

A mathematical model was developed that allows sample decay to be calculated if the temperature history of the sample is known.

Temperature specifications, and changes in the procedure necessary to eliminate the decay problem are proposed.

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SECTION I

INTRODUCTION

On April 30, 1971, the Environmental Protection Agency (EPA) promulgated in the Federal Register the national primary and secondary air quality standards for sulfur dioxide (SO_2). At the same time, the reference method for the determination of ambient concentrations of SO_2 was also described.[1]

Previous research[2] on the SO_2 reference method indicated that a stable complex was formed when SO_2 in the ambient air was collected in a solution of potassium tetrachloromercurate and subsequently analyzed for SO_2 concentration with formaldehyde and pararosaniline. The complex formed, dichlorosulfitomercurate (SO_2-TCM), had suspected thermal instability[3] (1 percent per day at 22°C), but sample refrigeration at 5°C resulted in no decay for up to 30 days.

With the completion of two collaborative tests[4,5] of the SO_2 reference method, no indication of any major effect of thermal instability was found. This was due mostly to the experimental design of the tests, which did not address itself to elevated temperatures of sampling, shipment, and storage of SO_2-TCM samples prior to analysis.

At present, it is a common practice to sample for ambient concentrations of SO_2 in a thermostated sampling box (35°C) and then to transport the collected 24-hour SO_2 samples back to the laboratory for analysis in a non-temperature controlled container. This could involve either direct transportation of samples to the laboratory by staff personnel or transportation by the U.S. Posta Service. Upon receipt at the laboratory, the samples are stored either in the

dark at room temperature, or in a refrigerator. Thus, prior to analysis, the collected samples are exposed to a variety of temperature conditions for various lengths of time. Therefore, it became necessary to define the effect of temperature and time on the stability of SO_2-TCM samples, since it had never before been investigated at elevated temperatures.

SECTION II

EXPERIMENTAL

The specific reagents and procedures used for sample preparation and analysis are those specified in the Federal Register for the determination of SO_2 in the atmosphere (Pararosaniline Method).[1] Other pertinent experimental details not contained in that procedure are described in the following sections:

SAMPLE PREPARATION

Sufficient quantities of five concentrations of SO_2 in TCM (0, 0.2, 0.4, 0.8, and 1.6 μg SO_2/ml) were prepared by dilution of an SO_2-TCM stock standard prepared from sodium metabisulfite. Four sets of the five different concentrations were prepared by filling (~ 80 ml) each 100-ml polypropylene centrifuge tube with a specific concentration and capping it with a polypropylene tube closure. This is the same tube and closure recommended[1] for use when sampling for SO_2 in the ambient air for 24 hours.

TEMPERATURE CONTROL

Each set of tubes was placed in a constant temperature bath. Each bath was thermostated at either 20, 30, 40 or 50°C. The specific temperature was maintained within ± 0.1°C. Each tube was submerged below the solution volume line.

SAMPLE ANALYSIS

After selected periods of time, portions of the thermostated samples were taken, and rapidly cooled to 20°C in a constant temperature bath to prevent further decay before analysis. Aliquots of these portions were analyzed immediately for SO_2 concentration by the SO_2 reference method. This temperature (20°C) was also the temperature used for dye formation in the analysis part of

the procedure.

DATA ANALYSIS

Best fit regression analyses and equations were derived using a programmable calculator-plotter.

SECTION III

RESULTS AND DISCUSSION

In sampling and analysis of ambient concentrations of SO_2 by the Federal Register method, there were two areas where temperature and length of exposure to various temperatures needed investigation. These areas were: (1) the effect of temperature on the ability to collect a valid sample and (2) the effect of temperature on the stability of the collected sample. We chose the second area for our investigations, assuming that if the decay is substantial at higher temperatures, we would need to define it statically before any investigation of the dynamic collection system could be attempted. This report then discusses only area two.

To define the effect of temperature on the determination of ambient concentrations of SO_2 collected in 0.04 M TCM, we needed to investigate four areas: (1) the reaction rate at which the SO_2-TCM complex is decaying with time at a specific ambient temperature, (2) the reaction order indicating how the reaction rate varies with SO_2 concentration, or with another species present, (3) a general outcome (decay) when any concentration of SO_2 in TCM is exposed to elevated ambient temperatures, and (4) a method to estimate the effect of sample exposure to varying temperature.

RATE OF REACTION

The rate of reaction (decay) of the SO_2-TCM complex was determined by analyzing aliquots of the thermostated samples for SO_2 concentration by the SO_2 reference method, at various periods of time, and then plotting the data to derive a best fit regression equation (Figures 1 to 4). Using this technique the slope of the curve described the rate of decay. The general

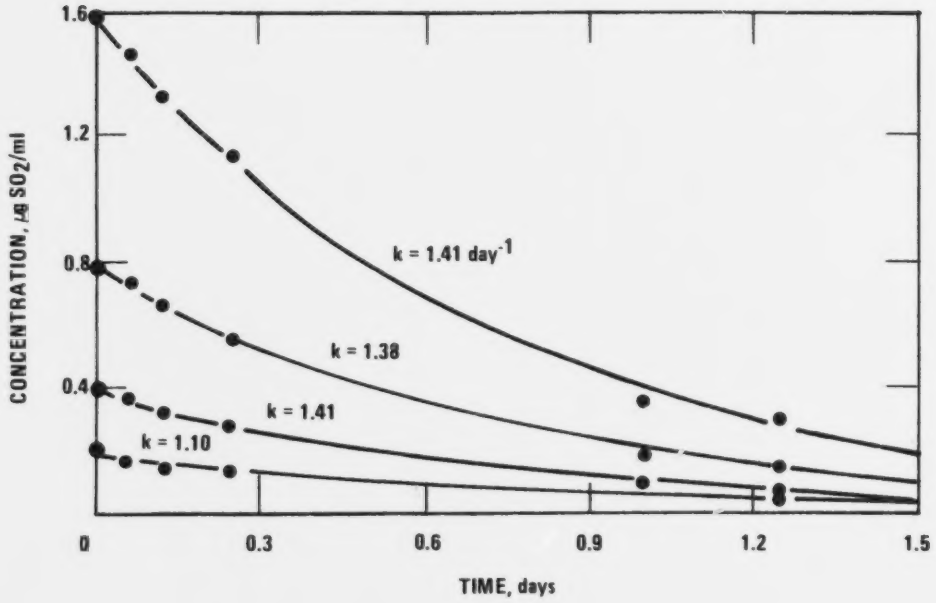

Figure 1. Effect of temperature on stability of dichlorosulfitomercurate complex, 50°C.

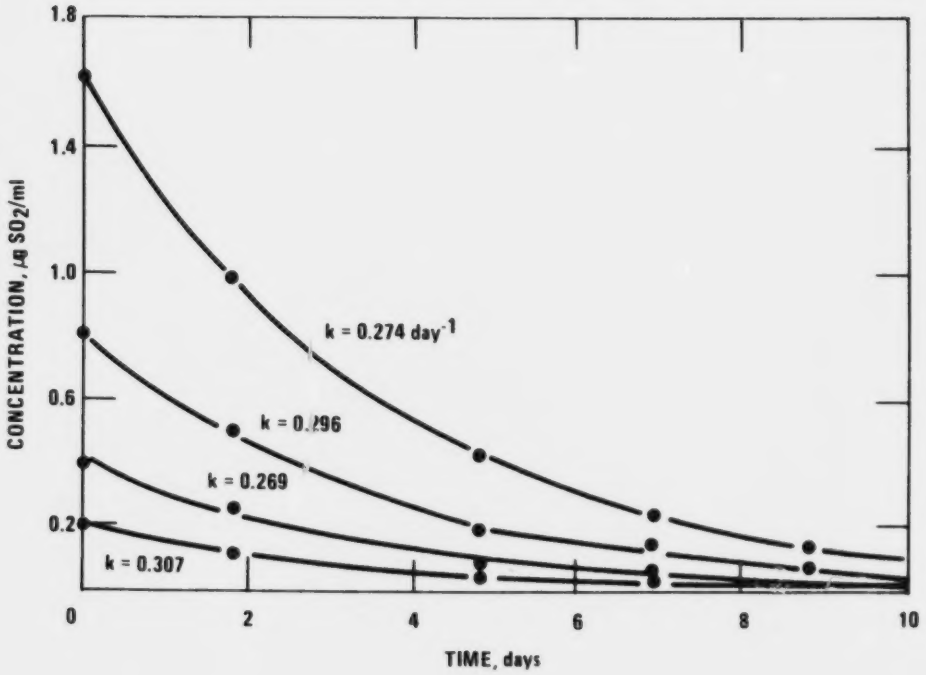

Figure 2. Effect of temperature on stability of the dichlorosulfitomercurate complex, 40°C.

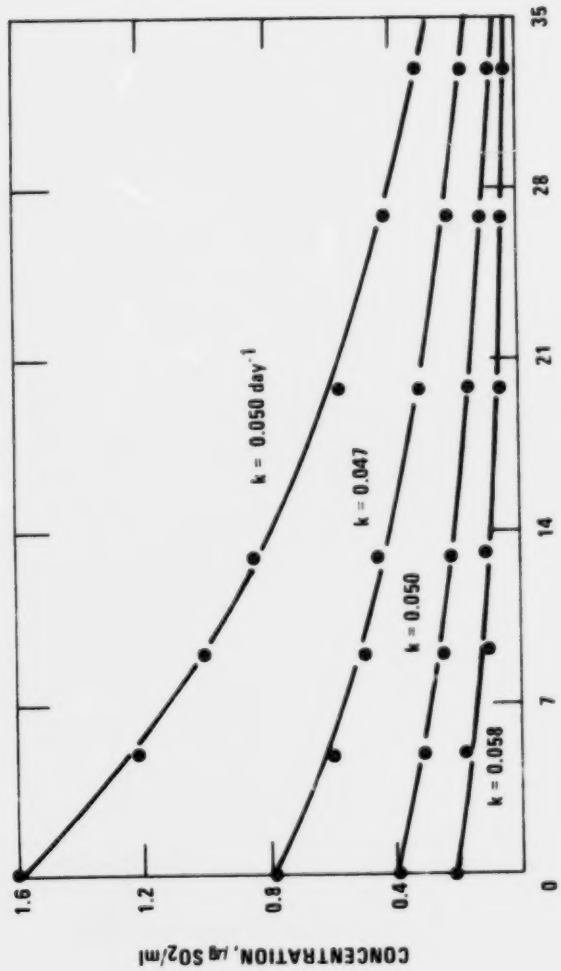

Figure 3. Effect of temperature on stability of dichlorosulfitomercurate complex, 30°C.

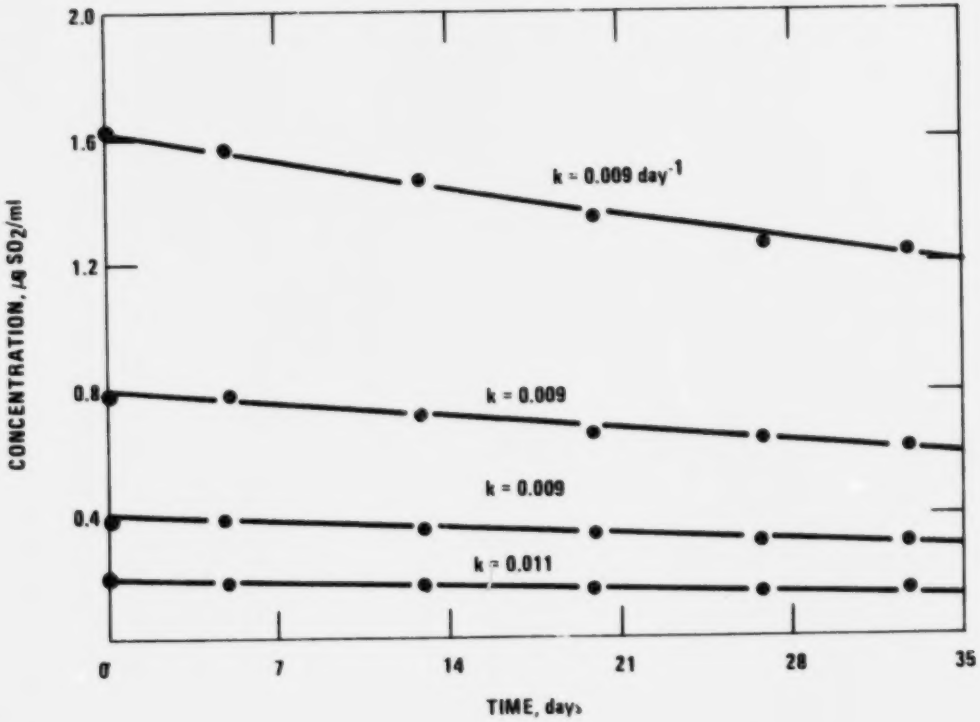

Figure 4. Effect of temperature on stability of dichlorosulfitomercurate complex, 20°C.

equation best fitting these data is described by an exponential curve of the formula

$$C = Ae^{-kt} \qquad (1)$$

where

C = concentration measured, μg SO_2/ml

A = a constant, μg SO_2/ml

k = rate of decay, day^{-1}

t = time, day

If we assume no decay has taken place at t = o(k = o), then C = A, which defines A as the initial concentration, C_o, and the equation

$$C = C_o e^{-kt} \qquad (2)$$

will describe the data.

Comparing the rates of decay at each temperature (20, 30, 40 and 50°C), we found the rate of decay at a given temperature to be independent of concentration in the range of 0.2 to 1.6 μg SO_2/ml. This represents a 24-hour SO_2 sample concentration of 35 to 278 μg SO_2/m^3 collected at a sample flow rate of 0.2 l/min.

The rate of decay of the 0.2 μg SO_2/ml sample at 50°C differs slightly from the other rates of decay at that temperature. This effect is also evident at the other temperatures, and is probably due to poor precision in the measurements at this low concentration. This is evident when one considers that the minimum sensitivity is approximately 0.14 μg SO_2/ml and that small net losses (< 0.14 μg/ml) are being measured at this concentration.

By determining an average rate of decay ($\bar{k}$) at each temperature, we can describe decay per day of a collected SO_2-TCM sample at a specific temperature (Table 1) with the equation

$$P = 100\ (1-e^{-kt}) \qquad (3)$$

where

P = percent decay/day

100 = conversion factor

$\bar{k}$ = average rate of decay, day^{-1}

t = time of exposure to a specific temperature, day

The data in Table 1 indicate that, with this reaction, the average rate of decay ($\bar{k}$) increases about 5-fold for each 10°C rise in temperature.

ORDER OF REACTION

Although our data indicated exponential decay and therefore, a first order reaction, we applied the Van't Hoff equation[6] to the data as an independent means of determining the order of the decay reaction. Van't Hoff stated that the true order of reaction can be determined using a log-log plot of the velocity of the reaction against different initial sample concentrations at a specific temperature, e.g.

$$V = kc^n \qquad (4)$$

$$\ln V = \ln k + n \ln c \qquad (5)$$

where:

ln = logarithm, base e

V = velocity of reaction, µg SO_2/ml-day

k = rate of reaction, day^{-1}

n = order of reaction (slope of line)

c = concentration of sample, µg SO_2/ml

Table 1. EFFECT OF TEMPERATURE ON PERCENT DECAY PER DAY

Temperature, °C	Average rate constant of decay ($\bar{k}$)	Percent loss per day
20	0.009 day^{-1}	0.9
30	0.051 day^{-1}	5.0
40	0.287 day^{-1}	25.0
50	1.33 day^{-1}	73.6

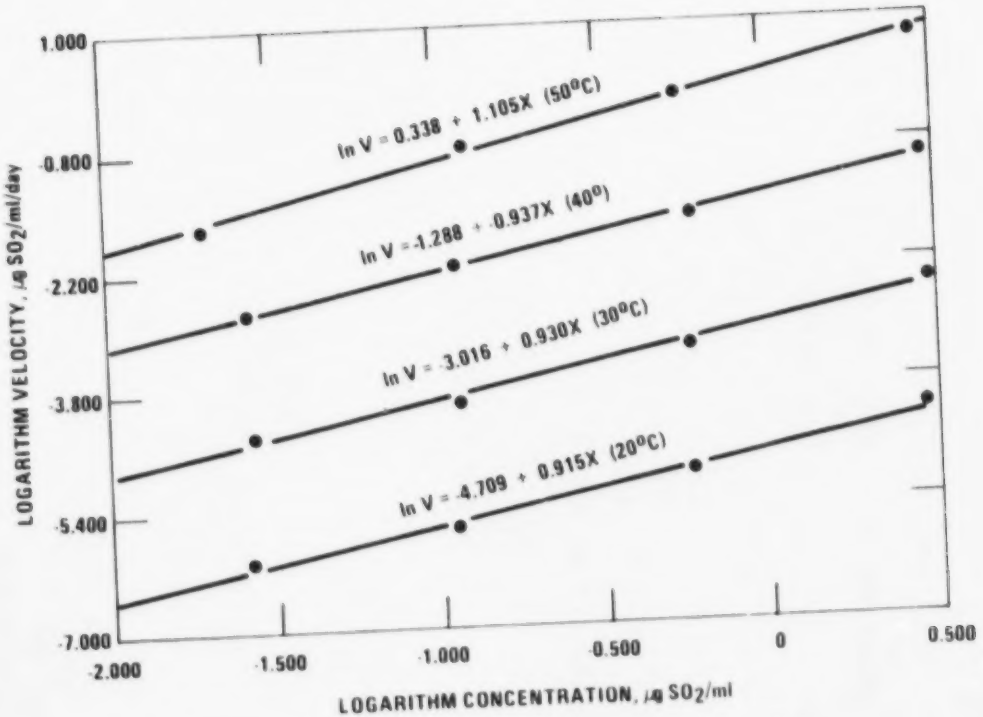

Figure 5. Determination of order and rate of reaction.

If this plot gives a straight line, then the slope of the line is an estimate of the order of the reaction with respect to initial sample concentration and the y-intercept is an estimate of the logarithm of the rate of decay. Our data indicate that the average order of reaction is 0.97 (Figure 5), thus confirming that the decay reaction is first order.

GENERAL OUTCOME (DECAY)

Arrhenius[7] showed that for certain reactions there is a linear relationship between the logarithm of the reaction rate (decay in this case) and the inverse of the absolute temperature at which the rate was measured. Therefore, by determining rates of decay at a few specific temperatures, we can derive an equation that will describe the rate of decay at any temperature within the range measured.

After determining the average rates of decay at 20, 30, 40 and 50°C, we used the Arrhenius equation (given below) to calculate an expression that would describe the rate of decay at any temperature within this range.

$$k = Ae^{-E/RT} \tag{6}$$

where

k = rate of reaction (decay), day^{-1}

A = frequency factor day^{-1}

E = energy of activation, calories/mole

R = gas constant, 1.987 calories/degree-mole

T = absolute temperature of reaction, °K

Taking logarithms, we have the expression

$$\ln k = \ln A-(E/R)(1/T) \tag{7}$$

which has the form $Y = b + mx$

A plot of this equation, using the above decay data, is shown in Figure 6.

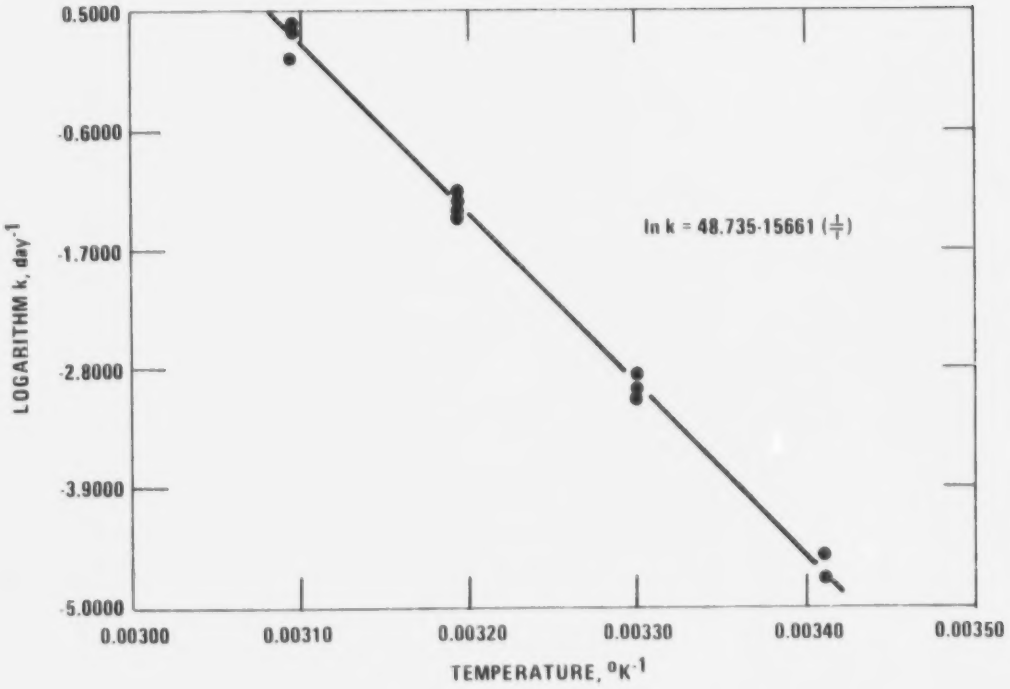

Figure 6. Effect of temperature on decay rate constant of dichlorosulfito mercurate complex.

An Arrhenius equation will hold only if the activation energy remains independent of temperature. This is the case as indicated by the linear relationship shown in Figure 6 where

$$\ln k = 48.735\text{-}15661 \left(\frac{1}{T}\right) \quad (8)$$

This equation can now be used to calculate the rate of decay at any temperature within the range 20 to 50°C and to estimate the rate of decay outside this range.

This equation also indicates that the energy of activation of the decay reaction is 31.2 kcal/mole.

Scaringelli[3] found that at 22°C, the SO_2-TCM complex decayed at the rate of 1.0 percent per day and could be stored at 5°C for up to 30 days without any noticeable decay. Using equation (8) we find that at 22°C the rate of decay is 1.3 percent per day and at the end of 30 days at 5°C a sample will have decayed a total of only 1.5 percent. Thus, the current study confirms the values previously reported.

EFFECT OF VARYING TEMPERATURE

Because field samples are exposed to different temperatures for various periods of time, a mathematical model was developed to estimate total decay that would be experienced under varying but known temperature conditions.

Using equation (2) and breaking the time of exposure (t) into parts of a day, we have

$$C_m = C_o e^{-[(k_1 t_1)_{T_1} + (k_2 t_2)_{T_2} + (k_3 t_3)_{T_3} + \ldots (k_i t_i)_{T_i}]} \quad (9)$$

taking logarithms, we have

$$\ln C_m = \ln C_o - [(k_1 t_1)_{T_1} + (k_2 t_2)_{T_2} + (k_3 t_3)_{T_3} + \ldots (k_i t_i)_{T_i}] \quad (10)$$

$$\ln C_m = \ln C_o - [\Sigma(k_i t_i)]_{T_i} \quad (11)$$

where

C_m = concentration measured, μg SO_2/ml

C_o = initial concentration, μg SO_2/ml

k_i = rate of decay at a specific temperature, day^{-1}

t_i = time of exposure to a specific temperature, day

T_i = a specific temperature, °K

Thus, by using the Arrhenius equation, we can determine the decay rate (k_i) for any temperature (T_i). By knowing the time of exposure (t_i) to a particular temperature, we can determine the overall effect of varying temperature on sample concentration. As practical examples of the use of this equation, we have estimated the decay of collected SO_2-TCM samples on exposure to the temperature conditions of a typical spring and summer day at the Research Triangle Park. If the initial concentration C_o is set equal to 1.0 μg SO_2/ml (174 μg SO_2/m^3), C_m will also represent the fraction of SO_2 remaining after decay for any concentration of SO_2 exposed to these conditions. The calculations are:

Temperature Conditions, Spring Day	k_i	$k_i t_i$
16 hours at 22°C (72°F)	0.013	0.009
4 hours at 25°C (77°F)	0.023	0.004
4 hours at 30°C (86°F)	0.054	0.009
	$[\Sigma(k_i t_i)]_{T_i}$ =	0.022

$$\ln C_m = 0\text{-}0.022 = -0.022$$

$$C_m = 0.978 \text{ µg } SO_2/\text{ml}$$

or a sample decay of 2.2 percent per day

Temperature Conditions, Summer Day	k_i	$k_i t_i$
16 hours at 22°C (72°F)	0.013	0.009
4 hours at 30°C (86°F)	0.054	0.009
4 hours at 35°C (95°F)	0.124	0.021

$$[\Sigma(k_i t_i)]_{T_i} = 0.039$$

$$\ln C_m = 0\text{-}0.039 = -0.039$$

$$C_m = 0.962 \text{ µg } SO_2/\text{ml}$$

or a sample decay of 3.8 percent per day.

These examples are intended to show the weighted effect, of even short-time exposure to temperature of 35°C or above on the overall decay rate experienced by SO_2-TCM samples.

SECTION IV

CONCLUSIONS

The data generated in this study indicated that collected SO_2-TCM samples decay at a critical temperature-dependent rate. The rate of decay is much greater than had been suspected and follows first order reaction kinetics. If the temperature history of the collected sample is known, the decay can be determined and corrected for by use of a mathematical model.

Since the SO_2-TCM complex is formed during sampling, one would expect that elevated temperatures would also cause decay during sampling. This has recently been confirmed in our laboratory.

SECTION V

RECOMMENDATIONS

The EPA Reference Method for measurement of SO_2 has been shown to be a reliable procedure when used under more restrictive temperature conditions than those in common field practice today.[4,5] Therefore, to maintain the integrity of field samples, we recommend that the solution temperature be kept at 25°C or less during sampling and at 5°C throughout shipment and storage prior to analysis. To meet these more restrictive temperature specifications, the following techniques are suggested as possible solutions.

REDESIGN OF GAS SAMPLER AND SHIPPING CONTAINER

This technique will in fact solve the decay problem altogether, if the more restrictive temperature specifications mentioned above are met. Physically separating the pump from the sampler, maintaining the temperature inside the sampler below 25°C year-round and shipping the samples in a refrigerated container will help meet these specifications.

RELOCATION OF SAMPLING SITE

If the sampling site could be relocated into an air conditioned room (22°C) and the sample maintained at room temperature, no significant decay would take place during sampling. After sampling, the samples must still be placed in a 5°C chamber during shipment and storage prior to analysis. This solution would presumably require relocating a large number of sampling sites.

CONTINUOUS MONITORS

The use of continuous monitors would provide no possibility for sample decay and also would give short-term pollutant profiles, but the initial cost per site would be high. The instrument would also require temperatures of approximately 22°C year-round for proper operation.

SAMPLE OF KNOWN CONCENTRATION

Instead of minimizing decay by temperature control, the decay can be measured and corrected by exposure of a sample of known concentration to the same environmental conditions as the field sample. This technique could be used to determine sample decay after collection, but would not provide an accurate measure of decay during sampling, because the concentration of the field sample is unknown and changing during sampling.

SECTION VI

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